Short communication

A lithium sulfur battery with high power density

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HIGHLIGHTS

- Sulfur content in the positive composite electrodes was 50 wt%.
- There was a correlation between surface area of the carbon and utilization of sulfur.
- Reversible capacity of over 1600 mAh g^{-1} was obtained after 100 cycles at 1C at 25 °C.
- The positive composite electrode exhibits a power density of 11000 W kg^{-1} at 25 °C.

ARTICLE INFO

ABSTRACT

The performance of all-solid-state lithium sulfur (Li/S) batteries is investigated for some types of conductive materials. The surface area of the conductive material is found to have a greater influence on the battery performance compared with its electronic conductivity. All-solid-state Li/S cells prepared using a positive activated-carbon-based composite electrode exhibit an excellent cycling performance with a reversible capacity of over 1600 mAh g^{-1} after 100 cycles at 1.3 mA cm^{-2} (1C) at 25 °C. Furthermore, the positive composite electrode exhibits a high power density of over 11000 W kg^{-1} at 50% state of charge.

1. Introduction

High-capacity rechargeable batteries are in demand for future portable electronic devices, electric vehicles, and large-scale electricity storage. Lithium sulfur (Li/S) battery is regarded as one of the most promising systems for next-generation batteries because of its high theoretical capacity [1]. In addition, sulfur is an abundant and cheap material. However, the utilization of a sulfur electrode is not sufficient to achieve the theoretical capacity because sulfur's ionic and electronic conductivities are low. Furthermore, the cycling performance rapidly decreases because polysulfides formed during battery operation are highly soluble in the liquid electrolytes [2].

Many researchers have focused on confining the sulfur materials into porous nanostructures to prevent the dissolution of lithium polysulfides during charge–discharge reactions [3]. A few researchers have investigated ionic liquids that practically do not dissolve lithium polysulfides [4]. However, none of them has been able to completely inhibit the dissolution of polysulfides.

The use of an inorganic solid electrolyte (SE) (instead of organic liquid or ionic liquid electrolyte) is basically an effective approach to inhibit the dissolution of polysulfides. There are various inorganic SEs such as Li$_2$S–SiS$_2$, Li$_2$S–P$_2$S$_5$, and Li$_4$GeS$_4$–Li$_3$PS$_4$ with a high lithium-ion conductivity of over 10^{-4} S cm^{-2} at 25 °C [5–8]. All-solid-state Li/S batteries containing these SEs exhibit an excellent cycling performance because polysulfide dissolution is completely inhibited [9]. However, in many reports, the sulfur contents in the positive electrodes are still insufficient or the current density is too small for practical uses [10]. Therefore, the energy densities of these Li/S batteries are relatively low under practical current–density conditions.

In a recent report, we discussed the relationship between the P/S (number of P atoms/number of S atoms) ratio in SEs and the capacity and potential of all-solid-state Li/S batteries to improve the battery performance focusing on the reactivity of sulfur. The possibility of obtaining a high-energy-density battery was shown [11].

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In this report, we investigated the relationship between the properties of the conductive material and battery performance to further improve the efficiency of the devices. We found that the surface area of the conductive material has a greater influence on the battery performance compared with its electronic conductivity.

2. Experimental

2.1. Solid electrolyte (SE; $Li_{1.5}PS_{3.3}$)

Reagent-grade Li_2S (Furuuchi Chem. 99.9%) and P_2S_5 (Aldrich, 99%) were used as the starting materials [8]. The SE was prepared by the mechanochemical method using a planetary ball mill apparatus (Fritsch Pulverisette 7). The mechanochemical treatment was performed on a mixture of Li_2S and P_2S_5 (at a molar ratio of 60:40) using a ZrO_2 pot and balls.

2.2. Positive composite electrodes

Several positive composite electrodes containing elemental sulfur as the active material were prepared by ball milling using a planetary ball mill apparatus under an Ar atmosphere [9]. Reagent-grade sulfur (Aldrich, 99.5%), an SE ($Li_{1.5}PS_{3.3}$), and the conductive materials acetylene black (AB, Denki Kagaku Kogyo), Ketjenblack (KB, Lion Co.), and activated carbon (AC, Kansai Coke and Chemicals Co., Ltd.) were used as the starting materials. The conductive materials had Brunauer–Emmett–Teller surface areas of 70, 1200, and 3000 m^2 g^{-1}, respectively. The weight ratio of sulfur, SE, and conductive material was fixed to 50:40:10. Here AB and KB are widely known as a conductive carbon, and therefore commonly, their electronic conductivities are extremely higher than activated carbon [12,13].

2.3. Electrochemical measurement

The electrochemical properties of the positive composite electrodes were investigated in an all-solid-state cell [14]. Two-electrode cells were assembled in a glove box filled with dry Ar using several composite electrodes as the positive electrode, Li–In alloys as the negative electrode, and $Li_{10}GeP_2S_{12}$ [7] as the solid electrolyte. The positive electrode powder (7.5 or 1.2 mg) and solid electrolyte powder (70 mg) were placed in a polycarbonate tube (diameter 10 mm) and pressed at 200 MPa to form a two-layered pellet. The negative electrode, formed by piling a Li foil on an In foil, was placed on the surface of the two-layered pellet, where the piled foils were in contact with the solid electrolyte. In this process, the Li and In foils formed a Li–In alloy layer. The thus obtained three-layered pellet was then sandwiched between two stainless steel rods, which served as current collectors. The Li/In molar ratio in the negative electrode was 0.79. It has been reported that if the molar ratio is kept below one, the potential of Li–In alloys remains constant at approximately 0.6 V (vs. Li) [15]. In our report, 0.6 was adopted as the potential difference between Li–In and Li.

Electrochemical tests were conducted at several constant current densities from 0.64 to 39 mA cm^{-2} at 25 °C in an Ar atmosphere using a charge–discharge measuring device, ACD-01 (Asuka electronic Co. Ltd.).

The measurement of power density was conducted with reference to the method of JEVS D713. The measurements were performed at several states of charge (SOC) values at ±5.0, 10, 15, 20, 25, and 30 mA for 10 s.

3. Results and discussion

The measurements shown in Figs. 1–4 are performed on a cell containing a 7.5 mg positive composite electrode. The cut-off
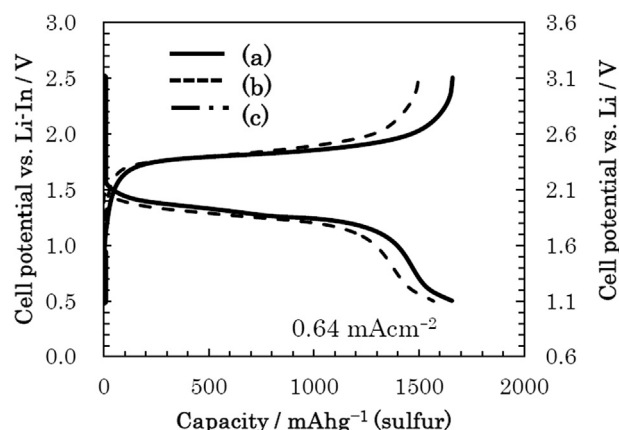

Fig. 1. Charge–discharge curves of all-solid-state lithium sulfur (Li/S) cells containing positive composite electrodes based on (a) AC, (b) KB, and (c) AB at 0.64 mA cm^{-2} at 25 °C.
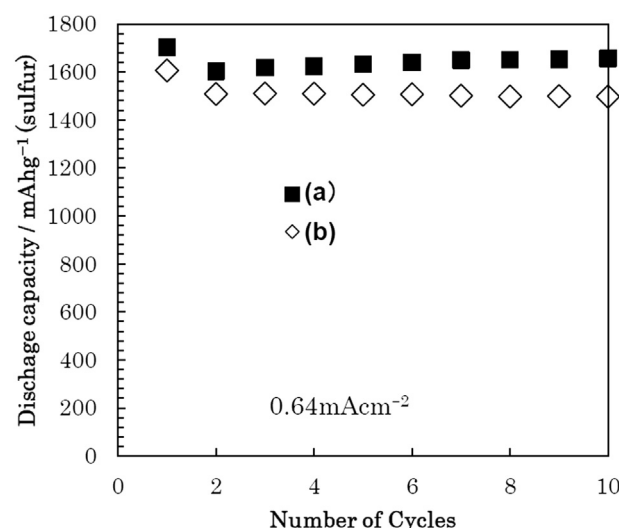

Fig. 2. Cycling performance of all-solid-state lithium sulfur (Li/S) cells containing (a) AC- and (b) KB-based positive composite electrodes at 0.64 mA cm^{-2} at 25 °C. The weight of the positive composite electrodes is 7.5 mg. The cut-off voltage is kept between 0.5 and 2.5 V (vs. Li–In).
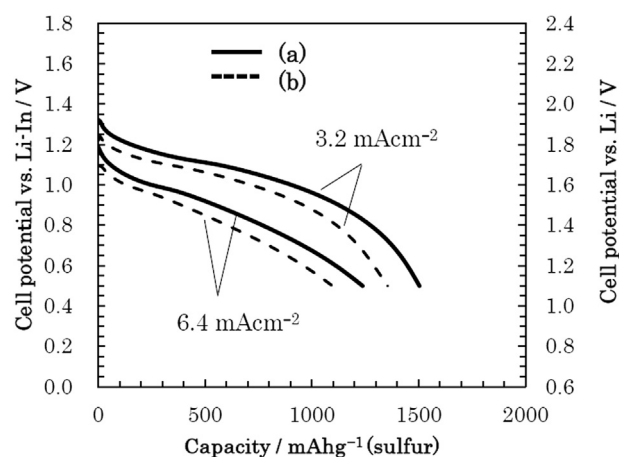

Fig. 3. Discharge curves of all-solid-state lithium sulfur (Li/S) cells containing positive composite electrodes based on (a) AC and (b) KB at current densities 3.2 and 6.4 mA cm^{-2} at 25 °C. The cut-off voltage is 0.5 V (vs. Li–In).
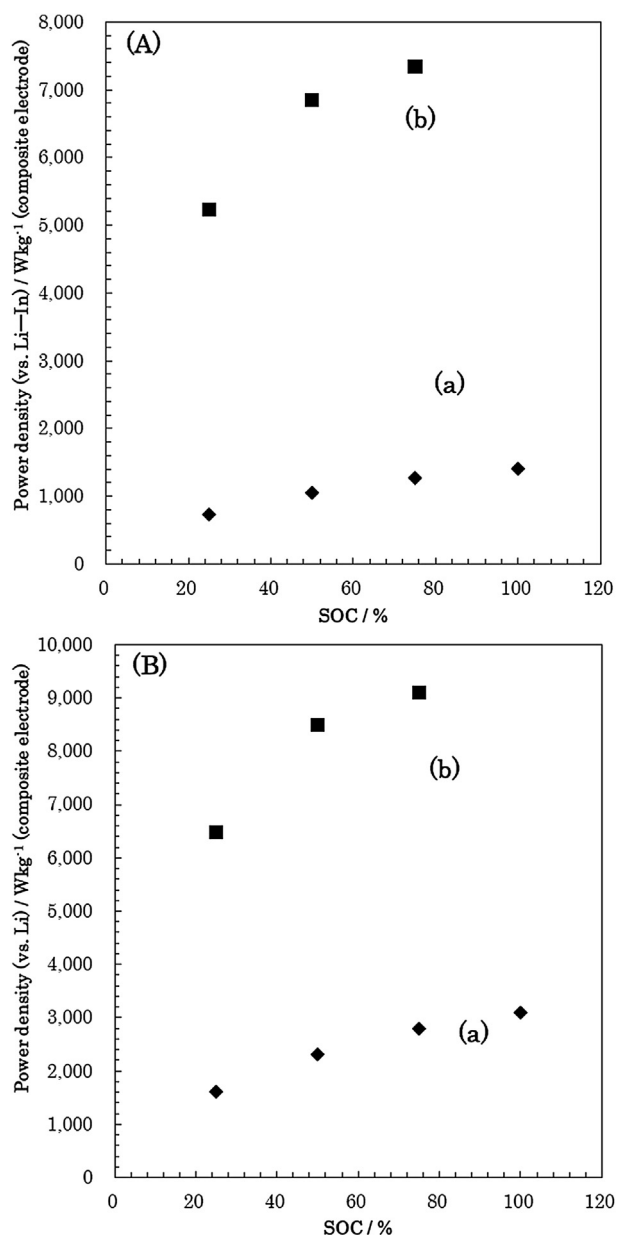
Fig. 4. Plot of the (a) power density and (b) regenerate power density at 25 °C calculated by (A) Li−In negative electrode, (B) metallic Li at different SOC for an AC-based positive composite electrode with a weight of 7.5 mg.

voltages are charged to 2.5 V (vs. Li−In) and discharged to 0.5 V (vs. Li−In).

Fig. 1 shows the charge−discharge curves of all-solid-state Li/S cells prepared using several positive composite electrodes at 0.64 mA cm^{-2} at 25 °C. Most cells behave as a secondary battery, except for the AB-based positive composite electrode. The capacity of the positive composite electrode using AB is less than 50 mAh g^{-1}, and extremely small to be confirmed in Fig. 1. The reason why this cell behaves differently is that the surface area of AB is too small to provide sufficient conductivity to the positive composite electrode. On the other hand, the cells of KB-based and AC-based positive composite electrode exhibit a plateau around 0.6 V (vs. Li−In); we presumed that this plateau corresponds to the reaction of SE in our previous report [11].

The cycling performance of these cells at 0.64 mA cm^{-2} at 25 °C was good, particularly, the cell using the AC-based positive

composite electrode has a large reversible capacity of over 1650 mAh g^{-1} (based on the incorporated sulfur active material weight) or over 825 mAh g^{-1} (based on the incorporated positive composite electrode weight) after 10 cycles (Fig. 2) (unless otherwise noted, the capacities hereafter are normalized to the sulfur active material content within the positive composite electrode). This value is quite close to the theoretical capacity of sulfur, and 10% higher than that observed for the cell containing the KB-based positive composite electrode in spite of its low electronic conductivity, whereas the morphology and particle size of these composite electrodes have not confirmed a clear difference in the scanning electron microscope images (Fig. S1, see Supporting Information). Therefore, it can be considered that the utilization efficiency of sulfur is improved by the high surface area of AC since increases the contact between this conductive material and sulfur at nano region. In this case, the influence of the surface area of the conductive material on the battery performance is larger than that of its electronic conductivity.

Fig. 3 shows the discharge curves of all-solid-state Li/S cells containing AC- and KB-based positive composite electrodes under current densities of 3.2 and 6.4 mA cm^{-2} at 25 °C after full charge, the cut-off voltage being 0.5 V (vs. Li−In). The AC-based positive composite electrode always has larger capacity and higher discharge potentials at the two investigated current densities, in spite of its lower electronic conductivity compared with KB-based positive composite electrode. The capacities of the AC-based positive composite electrode at 3.2 and 6.4 mA cm^{-2} at 25 °C are 1503 and 1238 mAh g^{-1}, respectively. These values are higher than the 1355 and 1096 mAh g^{-1} capacities observed for KB-based positive composite electrode, and the value is extremely large even at a high current density. The AC-based positive composite electrode also exhibits a good rate performance.

Short-term output characteristic is one of the very important properties in required battery performance, and therefore, the power density and regenerative power density of AC-based positive composite electrode at several SOC at 25 °C were shown in Fig. 4. Both parameters are determined with reference to JEVS D 713 Measurements are performed at several SOC of ±5.0, 10, 15, 20, 25, and 30 mA for 10 s. The power density and regenerate power density increase with increasing SOC. Here, the measurement and calculation of the power density are explained in detail. Fig. 5 shows a plot of the cell potential measured at 10 s at different current values. The value of current I_d corresponding to the lower limit cell potential of discharge was determined by the least squares method, which is shown in Fig. 5. The power density is calculated by [lower-limit cell potential (0.5 V vs. Li−In)] × I_d/ [weight of the positive composite electrode (in this case, 7.5 mg)]. Similarly, the value of current I_c corresponding to the higher limit cell potential of charge is determined by the least squares method. The regenerative power density is calculated by: [higher-limit cell potential (2.5 V vs. Li−In) × I_c/[weight of the positive composite electrode]. In Fig. 4(A), power density of the positive composite electrode is 1100 W kg^{-1} when Li−In alloy is used as the negative electrode at 50% SOC; the regenerative power density is 6900 W kg^{-1}. In Fig. 4(B), when metallic Li is used as the negative electrode, the power density of the positive composite electrode is calculated to be 2300 W kg^{-1} at 50% SOC; the regenerative power density is 8500 W kg^{-1} in this case. These values were relatively high; however, we think that they are insufficient for high power use as electric vehicle.

Therefore, the weight of the positive composite electrode was decreased from 7.5 mg to 1.2 mg to improve the battery performance by shortening the movement distance of lithium ions in the positive composite electrode; the battery performance of these cells is shown in Figs. 6 and 7.
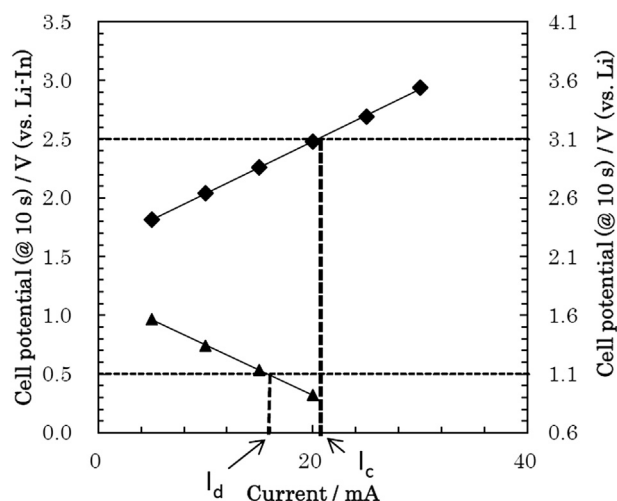
Fig. 5. Plot of the cell potential measured at 10 s at currents of ±5.0, 10, 15, 20, 25, and 30 mA. I_d and I_c, corresponding to the lower- and higher-limit cell potentials of charge, were determined by the least squares method. I_d: value of current corresponding to the lower limit cell potential of discharge. I_c: value of current corresponding to the higher limit cell potential of charge.

Fig. 6 shows the cycling performance of all-solid-state Li/S cells containing an AC-based positive composite electrode at 1.3 mA cm^{-2} at 25 °C. The current density corresponds to 1 C. The cut-off voltages are charged to 2.5 V (vs. Li–In) and discharged to 0.5 V (vs. Li–In).

The capacity of the positive composite electrode is above 1600 mAh g^{-1} after 100 cycles while the current density is relatively high and coulombic efficiency is approximately 100% during 100 cycles. The cell exhibits an excellent cycling performance for normal use.

The power density and regenerative power density of AC-based positive composite electrode at several SOC at 25 °C is shown in Fig. 7. Both parameters are determined following the same procedures described for Figs. 4 and 5. In Fig. 7(A), the power density of the positive composite electrode is 5100 W kg^{-1} when Li–In alloy is used as the negative electrode at 50% SOC; the regenerative power density is 35000 W kg^{-1}. In Fig. 7(B), when metallic Li is used as the negative electrode, the power density of the positive composite electrode is calculated to be 11000 W kg^{-1} at 50% SOC; the
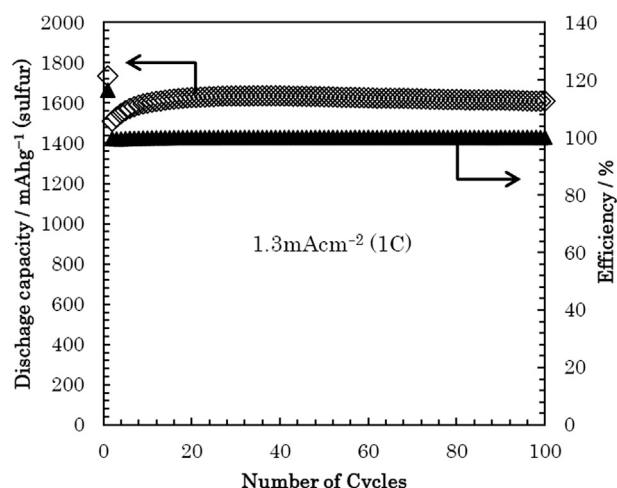

Fig. 6. Cycling performance of all-solid-state lithium sulfur (Li/S) cell containing an AC-based positive composite electrode at 1.3 mA cm^{-2} (1C) at 25 °C. The weight of the positive composite electrode is 1.2 mg. The cut-off voltage is kept between 0.5 and 2.5 V (vs. Li–In).
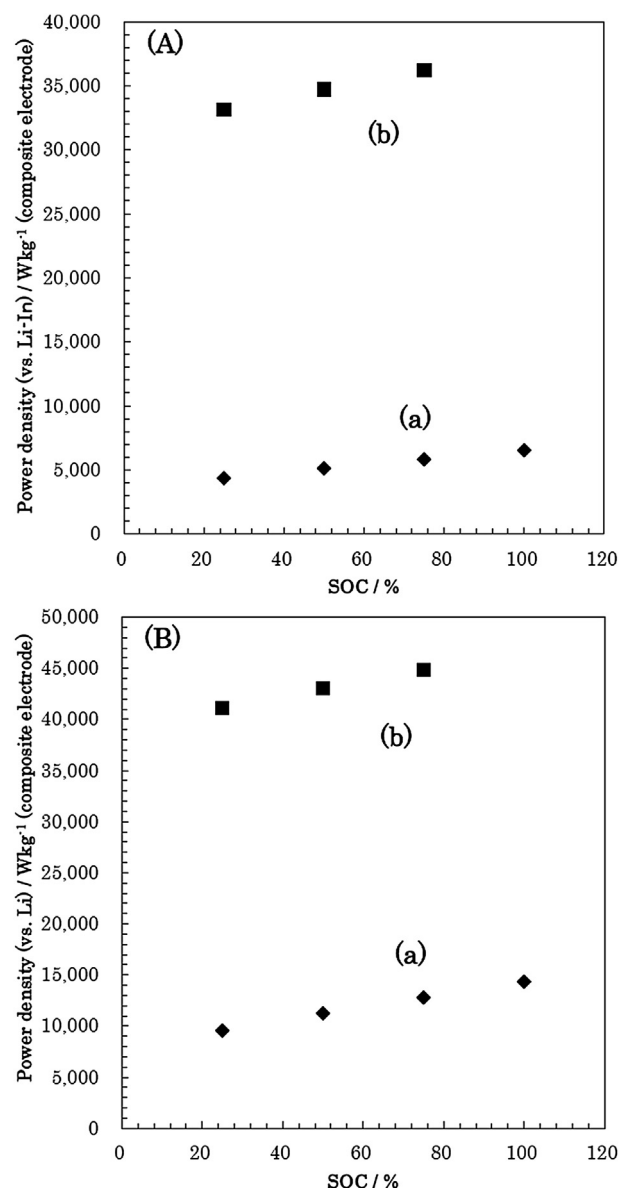

Fig. 7. Plot of the (a) power density and (b) regenerate power density at 25 °C calculated by (A) Li–In negative electrode, (B) metallic Li at different SOC for an AC-based positive composite electrode with a weight of 1.2 mg.

regenerative power density is 43000 W kg^{-1} in this case. This value is extremely higher than that in case of positive composite electrode with a weight of 7.5 mg; therefore, we observed that the power density was strongly dependent on thickness of positive composite electrode. This is an extremely high power density; therefore, the studied positive composite electrodes can be considered to have suitable power properties for use in electric vehicles.

4. Conclusions

The relationship between conductive material and battery performance was investigated to improve the efficiency of Li/S batteries. We found that the specific surface area of the conductive material has a greater influence on the battery performance compared with its electronic conductivity.

Positive composite electrodes containing AC with a high surface area exhibited extremely large reversible capacity above

1600 mAh g^{-1} at 1.3 mA cm^{-2} (1C) at 25 °C after 100 cycles and a high power density above 11000 W kg^{-1}. The power density and capacity observed for these electrodes are high enough for potential electric-vehicle applications.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.04.106.

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